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14. ABSTRACT Only three well characterized stable nitrogen fluoride oxide molecules, FNO, FNO ₂ and NF ₃ O, and one ion, NF ₂ O ⁺ , are known in which the fluorine and oxygen atoms are directly bonded to the nitrogen atom. ^[1] In this paper, we report the synthesis and characterization of N ₃ NOF ⁺ , a novel stable nitrogen fluoride oxide cation which can exist in the form of two different configurational isomers.					
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Synthesis and Characterization of $z\text{-N}_3\text{NFO}^+$ and $e\text{-N}_3\text{NFO}^+$ ** (PREPRINT)

*William W. Wilson, Ralf Haiges, Jerry A. Boatz, and Karl O. Christe**

Dedicated to Professor Dieter Naumann on the occasion of his 65th birthday.

Only three well characterized stable nitrogen fluoride oxide molecules, FNO, FNO₂ and NF₃O, and one ion, NF₂O⁺, are known in which the fluorine and oxygen atoms are directly bonded to the nitrogen atom.^[1] In this paper, we report the synthesis and characterization of N₃NOF⁺, a novel stable nitrogen fluoride oxide cation which can exist in the form of two different configurational isomers.

Our recent synthesis^[2] of the N₅⁺ cation [Eq. (1)]



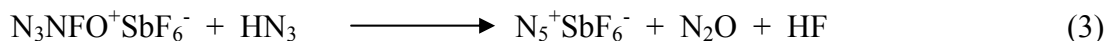
prompted us to explore the reactions of similar cations with HN₃. A logical candidate for this type of chemistry was the NF₂O⁺ cation.^[3-5] When NF₂O⁺SbF₆⁻ was combined with a stoichiometric amount of HN₃ in anhydrous HF solution between -45 °C and room temperature, one of the fluorine ligands was replaced by an azide group [Eq. (2)].



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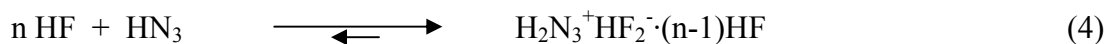
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The use of excess HN_3 under these conditions led to the formation of $\text{N}_5^+\text{SbF}_6^-$ and N_2O [Eq. (3)].



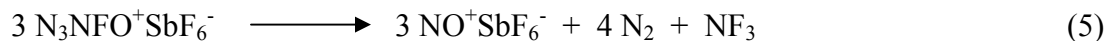
The mechanism of (3) was studied experimentally by ^{15}N isotopic substitution and theoretical calculations and involves the intermediate formation of the N_7O^+ cation. The chemistry taking place in the $\text{NF}_2\text{O}^+/\text{HN}_3$ system, however, is considerably more complex than that given by Eqs. 2 and 3 and will be reported in a separate publication.

It was also found that, in anhydrous HF solution, HN_3 is completely protonated [Eq. (4)].



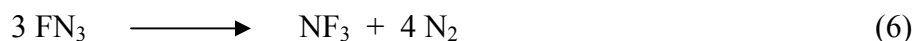
The formation of the H_2N_3^+ cation^[6] was confirmed by Raman and nitrogen-NMR spectroscopy. It is in accord with a previous report that HN_3 and HF have similar acidities and are capable of displacing each other from their salts.^[7] Because polymeric HF is a significantly stronger Lewis acid than monomeric HF,^[8] the equilibrium (4) is shifted all the way to the right side.

The $\text{N}_3\text{NFO}^+\text{SbF}_6^-$ salt is a white solid which is stable at room temperature and is highly soluble in anhydrous HF. It does not detonate when either struck with a hammer or being scraped with a metal spatula, and deflagrates when heated in an open flame. It ignites ethanol, reacts violently with water, and oxidizes bromide to bromine. Its general properties somewhat resemble those of $\text{N}_5^+\text{SbF}_6^-$.^[2] When heated to 50 – 60 °C, it decomposes mainly to $\text{NO}^+\text{SbF}_6^-$ with evolution of N_2 and NF_3 [Eq. (5)].



Reaction (5) was studied in solution by nitrogen NMR spectroscopy using N_3NFO^+ labeled in the α - and γ -positions with ^{15}N , resulting in the formation of ^{15}N labeled N_2 and

unlabeled NO^+ . It was also investigated by vacuum pyrolysis of the solid. The Raman spectrum of the solid residue showed $\text{NO}^+\text{SbF}_6^-$, and the infrared spectrum of the volatile products, trapped at $-196\text{ }^\circ\text{C}$, contained NF_3 . Reaction (5) most likely involves an intramolecular attack of the fluorine ligand of N_3NFO^+ on the electron-rich N_α atom of the azido group, accompanied by extrusion of the NO^+ cation. The intermediately formed FN_3 molecule can decompose under these conditions to N_2 and NF_3 [Eq. (6)].^[9]



In the $^{14/15}\text{N}$ and ^{19}F NMR and the Raman spectra of $\text{N}_3\text{NOF}^+\text{SbF}_6^-$, two sets of peaks were observed, suggesting the presence of two stereo isomers. This was confirmed by theoretical calculations at the B3LYP, MP2 and CCSD(T) levels of theory showing two catenated minimum energy structures of very similar energies ($\Delta E \leq 0.6 \text{ kcal mol}^{-1}$ at all levels of theory, with either one or the other isomer being favored depending on the level of calculation and basis set used). A third minimum energy structure was also found, derived from a five-membered N_4O ring with the fluorine atom attached to a nitrogen atom in α -position to the oxygen atom. However, its energy was $39.4 \text{ kcal mol}^{-1}$ higher than that of the catenated z -isomer at the B3LYP/6-311G(2df) level of theory. The geometries, obtained for the catenated z - and e -isomers at the CCSD(T)/6-311(2df) level, the highest level used in this study, are shown in Fig.1. At this level, the z -isomer is favored by $0.6 \text{ kcal mol}^{-1}$. Both structures are planar (symmetry C_s) and differ mainly in the relative positions of the F and the O atoms, with the remaining bond lengths and angles being very similar. In the z -isomer, the azido and the fluorine ligands are *cis* to each other, while in the e -isomer they are *trans* to each other.

The chemical shifts and coupling constants observed for both isomers in HF solution at $-30\text{ }^\circ\text{C}$ are summarized in Figure 2. As can be seen, the isomeric splitting is very large for the

fluorines ($\Delta\delta^{19}\text{F} = 98$ ppm) and decreases along the nitrogen chain with increasing distance from the fluorine atom ($\Delta\delta\text{N}_1 = 22$, $\Delta\delta\text{N}_\alpha = 11$, $\Delta\delta\text{N}_\beta = 3$, $\Delta\delta\text{N}_\gamma = 2$ ppm). The assignments to the two isomers were facilitated by the fact that they were present in a different ratio of 1 : 1.45 for the *z*- and *e*-isomer, by the observed coupling constants, theoretical calculations (the values calculated at the PBE1BPE/6-311+G(2df) level of theory are given in brackets in Figure 2), and by analogy to those known for similar covalent azides.^[10,11] For N_α and N_γ , they result in smooth trends when plotted against the electron withdrawing power of the X-group of X-N_3 , while the chemical shifts of N_β are randomly scattered around a value of 141 ± 28 ppm (Figure 3). The agreement between the observed and calculated trends in the nitrogen shifts is good, particularly if it is kept in mind that the accurate calculation of chemical shifts for nitrogens containing free valence electron pairs is difficult, unless extensive electron correlation treatment, such as that provided by the CCSD(T) method, is used.^[2] The fact that in HF solution at -30 °C the *e*-isomer is slightly favored over the *z*-isomer, is in contrast to our highest level prediction for the free gaseous ion at 0 K and can be attributed to either shortcomings of the computations and/or solvation or temperature effects.

The presence of an NFO group in each isomer is established by (i) the ^{19}F spectrum which shows two triplets of equal intensity with $^1J^{19}\text{F}^{14}\text{N}$ of 166.2 and 168.4 Hz and chemical shifts of 274.7 and 373.0 ppm, respectively, which are reasonable when compared to the NF_2O^+ signal, observed in this study under the same conditions at δ 325.2 ppm with $^1J^{14}\text{N}^{19}\text{F} = 259$ Hz; and (ii) the ^{14}N spectrum which shows two broad doublets at δ -59.5 and -81.1 ppm, respectively, with $^1J^{14}\text{N}^{19}\text{F} \sim 167$ Hz due to coupling with one fluorine atom. These values are again in good agreement with the nitrogen shift of -97.7 ppm observed for the NF_2O^+ cation.

Of the three nitrogen atoms of the azido group, only the N_β atoms were observable in the ^{14}N spectra at -167.4 and -170.6 ppm for the *e*-isomer and the *z*-isomer, respectively. For the observation of N_α (-127.8 ppm for *e*; -138.9 ppm for *z*) and N_γ (-80.1 ppm for *e*; -82.6 ppm for *z*) ^{15}N substitution was required. The observed nitrogen chemical shifts are consistent with the presence of a covalent azido group attached to a highly electronegative ligand (see Figure 3) and a nitrogen atom attached to a fluorine atom and an oxygen atom.

The second method of identification used for N_3NOF^+ was vibrational spectroscopy. The observed Raman and infrared spectra (see Tables 1 and 2) are in good agreement with the spectra calculated for the two isomers at the B3LYP, MP2 and CCSD(T) levels of theory. As expected, the CCSD(T) calculations resulted in the best fit with the observed spectra and, therefore, only these data have been included in the Tables.

As one might expect, the frequencies of the bands characteristic for the azido groups are similar to those observed in other covalent azides^[2,10] and, also, are similar for the two isomers. However, three of the modes, ν_2 , ν_5 , and ν_7 , which involve mainly motions of the FNO group, differ significantly and, in the two isomers, are separated by 47, 160 and 31 cm^{-1} , respectively, in HF solution and by 67, 174 and 26 cm^{-1} , respectively, in the solid state. Additional support for the predicted structures comes from the good agreement between observed and calculated isotopic shifts in $^{15}\text{N-N-N-NFO}^+$ and $\text{N-N-}^{15}\text{N-NFO}^+$ (see Tables 1 and 2).

The assignment of the vibrational spectra was tricky because of the presence of two isomers which could not be separated, some starting materials, such as $\text{NF}_2\text{O}^{+[3]}$ or $\text{H}_2\text{N}_3^{+[6]}$, and some decomposition products, such as $\text{N}_5^{+[2]}$, $\text{NO}^{+[12]}$ and $\text{NO}_2^{+[12]}$. A large number of spectra were recorded and the assignments to the two N_3NOF^+ isomers were based on the observed growth and decay patterns. A typical Raman spectrum is shown in Figure 4, where NF_2O^+ (A)

and NO_2^+ (B) were present as impurities. Whereas the 1407 cm^{-1} band of NO_2^+ and the 1869 and 1158 cm^{-1} bands of NF_2O^+ presented no problem, the 900 cm^{-1} band of NF_2O^+ fell right on top of the relatively weak ν_5 band of the *e*-isomer. The identity and relative intensity of the latter were confirmed by ^{15}N substitution in either the N_γ or N_α positions of the azido group, resulting in a 50/50 mix of the two isotopomers, $^{15}\text{N-N-N-NFO}^+$ and $\text{N-N-}^{15}\text{N-NFO}^+$. Both isotopomers shifted away from the unsubstituted NF_2O^+ peak and resulted in two well resolved Raman bands of equal intensity with a frequency separation of 18.7 cm^{-1} (calculated value = 18.5 cm^{-1}).

Because the identity of the vibrations in the 500 to 1200 cm^{-1} region was not obvious, normal coordinate analyses were carried out for both isomers. As can be seen from Tables 3 and 4, most of the normal modes are complex mixtures of the corresponding symmetry coordinates. For example, the N-F stretching motion in the *e*-isomer is distributed over several modes, with the highest contribution to a single mode, in this case ν_4 , being only 29%. Therefore, the assignment of characteristic modes, such as N-F stretching, to single frequencies and the comparison of such frequencies for the two isomers is unwarranted. Due to the large size of the A' blocks and the strong coupling, the determination of explicit F-matrices and internal force constants were not feasible.

In conclusion, the new nitrogen fluoride oxide cation, N_3NFO^+ , was prepared from NF_2O^+ and HN_3 and characterized by vibrational and multinuclear NMR spectroscopy and electronic structure calculations. The cation is planar and can exist in the form of two stereo isomers, depending on whether the azido group and the fluorine ligand are *cis* (*z*-isomer) or *trans* (*e*-isomer) with respect to each other. Although the azido groups in the two isomers are similar, the bond lengths and the ^{19}F chemical shifts of the N-F bonds in the two isomers differ significantly, with the *z*-isomer exhibiting the longer (by $.05\text{ \AA}$) bond.

Experimental Section

Caution! Neat HN_3 is highly explosive and should, whenever possible, be handled only in solution. Anhydrous HF can cause severe burns and contact with the skin must be avoided.

Materials and Apparatus: All reactions were carried out in Teflon-FEP or Kel-F ampules that were closed by stainless steel valves. Volatile materials were handled in a stainless steel/Teflon-FEP vacuum line.^[13] All reaction vessels were passivated with ClF_3 prior to use. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Raman spectra were recorded directly in the Teflon or Kel-F reactors in the range $4000\text{--}80\text{ cm}^{-1}$ on a Bruker Equinox 55 FT-RA spectrophotometer, using a Nd-YAG laser at 1064 nm. The infrared spectra were recorded on a Midac, M Series, FT-IR spectrometer using AgCl pellets. The pellets were prepared inside the glove box using an Econo mini-press (Barnes Engineering Co). The starting materials, $\text{NF}_2\text{O}^+\text{SbF}_6^-$ ^[3] and HN_3 ^[2] were prepared by literature methods. HF was dried by storage over BiF_5 .^[14]

Preparation of $\text{N}_3\text{NFO}^+\text{SbF}_6^-$. In a typical experiment, $\text{NF}_2\text{O}^+\text{SbF}_6^-$ (0.3 mmol) was added to a prepassivated, thin-walled, 5 mm o.d. Kel-F ampule, which was closed by a stainless steel valve. On the vacuum line, anhydrous HF (270 mg) was condensed in at $-196\text{ }^\circ\text{C}$ and the $\text{NF}_2\text{O}^+\text{SbF}_6^-$ was dissolved in the HF at room temperature. The ampule was cooled back to $-196\text{ }^\circ\text{C}$, and a mixture of HN_3 (0.3 mmol) and HF (750 mg) was condensed in. The resulting mixture was warmed to temperatures between -45 and $-20\text{ }^\circ\text{C}$, producing the desired $\text{N}_3\text{NFO}^+\text{SbF}_6^-$ salt in HF solution. If the neat solid was desired, all volatile material was pumped off at $-30\text{ }^\circ\text{C}$. The product was characterized by multinuclear NMR and vibrational spectroscopy.

Theoretical Methods: The molecular structures, harmonic vibrational frequencies, and infrared and Raman vibrational intensities were calculated using second order perturbation theory (MP2, also known as MBPT(2)^[15]), single- and double-excitation coupled cluster methods,^[16] including a non-iterative perturbative treatment of connected triple excitations (CCSD(T)),^[17] and also at the DFT level using the B3LYP hybrid functional,^[18] which included the VWN5 correlation functional.^[19] Hessians (energy second derivatives) were calculated for the final equilibrium structures to verify them as local minima; i.e., having a positive definite Hessian. The calculations were performed using the electronic structure codes GAMESS,^[20] Gaussian 98,^[21] and ACES II.^[22] The second derivatives were analyzed using the program BMATRIX.^[23]

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Keywords: Multinuclear NMR spectroscopy, nitrogen fluoride oxide cations, vibrational spectroscopy, stereo isomers, theoretical calculations

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Table 1. Observed and unscaled calculated vibrational frequencies [cm^{-1}] and intensities for $z\text{-N}_3\text{NOF}^{+a}$

mode	observed freq, cm^{-1} , rel int				calcd freq, (IR)[Ra] int ^b	
	Ra, HF sol,	Ra, solid,	IR, ^c solid,	$\Delta\nu$	CCSD(T)/6-31G(d)	$\Delta\nu$
	20 °C	20 °C	20 °C	$^{14}\text{N}/^{15}\text{N}^d$	$^{14}\text{N}^d$	$^{14}\text{N}/^{15}\text{N}^{d,e}$
a', ν_1	2253 [10]	2252 [10]	^f	32	2246 (27)[114]	33.2
ν_2	1771 [1.1]	1771 [.8]	1765 s	0	1810(387)[6.2]	0
ν_3	1159 [1.7]	1162 [1.8]	1156 vs	12-20 ^g	1201 (285)[49]	20.5
ν_4	979 [1]	980 sh, vw	994 ms		991(71)[.40]	13.3
ν_5	^h	733 [.8]	732 m		750 (58)[8.3]	4.4
ν_6	680 sh	683 [1]	ⁱ		669 (1.7)[9.3]	0.7
ν_7	546 [1.3]	548 [.6]	545 w		538 (6.7)[5.6]	1.3
ν_8	443 [0.6]	447 [0+]			436 (0.7)[.87]	0.6
ν_9	204 [4.4]	210 [1.5]			191 (1.1)[2.9]	2.4
a'', ν_{10}	^k	683 [1]	ⁱ		656 (9.3)[.77]	3.0
ν_{11}	461 [0.4]	465 [.3]			451 (3.8)[.59]	0
ν_{12}	140 sh	140 sh			142(0.37)[.24]	0.8

[a] The spectra were recorded for a mixture of the z - and the e -isomers; therefore, some of the observed relative intensities contain contributions from the other isomer, whenever their frequencies coincide; The Raman spectra were recorded over a temperature range of -110 to 20 °C; because the observed frequencies changed by less than 2 cm^{-1} for all bands, only the 20 °C data are listed; in addition to the bands due to the cations, the following bands were observed for SbF_6^- : Ra (HF): ν_1 , 654, vs; ν_2 , 571, w; ν_5 , 284, m; Ra (solid): 658, 567, 285 cm^{-1} ; IR (solid): ν_3 , 651 cm^{-1} ; [b] calculated IR and Raman intensities are given in km mol^{-1} and $\text{\AA}^4 \text{amu}^{-1}$, respectively; the Raman intensities were calculated at the MP2/cc-pvtz level; [c] the IR spectrum was recorded as a pressed AgCl disc; [d] frequency differences between the isotopomer containing ^{15}N in the N_α position and that containing ^{15}N in the N_γ position; [e] the calculated isotopic shifts were obtained at the B3LYP/aug-cc-pvdz level and scaled by the same factor by which the calculated frequencies deviated from the observed ones; [f] a strong band was observed at 2241 cm^{-1} with a shoulder on its high frequency side; decomposition studies showed that this band did not decay together with the other N_3NOF^+ bands and, therefore, is attributed to an unknown impurity; the high frequency shoulder probably represents ν_1 of the cation; [g] based on line width of poorly resolved band; [h] obscured by strong line from Teflon-FEP sample tube; [i] not observed because of interference from a Kel-F sample tube band; [j] obscured by ν_3 of SbF_6^- ; [k] obscured by ν_4 of SbF_6^- .

Table 2. Observed and unscaled calculated vibrational frequencies [cm^{-1}] and intensities for $e\text{-N}_3\text{NOF}^+$ ^a

mode	observed freq, cm^{-1} , rel int				calcd freq, (IR)[Ra] int ^b	
	Ra, HF	Ra, solid,	IR, ^c solid,	Δv	CCSD(T)/6-31G(d)	Δv
	sol, 20 °C	20 °C	20 °C	¹⁴ N/ ¹⁵ N ^d	¹⁴ N ^c	¹⁴ N/ ¹⁵ N ^{d,e}
a' v ₁	2253 [10]	2252 [10]	f	32	2249 (16)[126]	33.4
v ₂	1705 [0.7]	1704 [0.6]	1704 ms	0	1739 (273)[8.9]	0.5
v ₃	1159 [1.7]	1162 [1.8]	1156 vs	12-20 ^g	1210 (413)[44]	12.0
v ₄	991 [.9]	995 [1.3]	994 ms	10	1009 (12)[5.6]	9.8
v ₅	^h	901 [0.4]	903 m	18.7	885 (24)[7.2]	18.5
v ₆	668 [1]	672 [0+]	i		658 (14)[6.6]	0.8
v ₇	516 [.7]	519 [.6]	518 w		504 (5.3)[3.9]	1.8
v ₈	465 [0+]	465 [.4]	463 w		451 (1.7)[.95]	0.9
v ₉	180 sh	193 sh			177 (1.1)[4.2]	2.0
a'' v ₁₀	^k		i		675 (10)[.86]	1.5
v ₁₁		480 [0+]	477 vw		473 (1.5)[.39]	0.4
v ₁₂	140 sh	140 sh			159 (0.00)[.39]	0.8

[a]-[k] See footnotes [a]-[k] of Table 1.

Table 3. Results from the normal coordinate analysis of e -N₃NOF⁺ at the B3LYP/cc-pvtz level

calcd freq, cm ⁻¹	symmetry force constants ^a									PED [%] ^b
	F ₁₁	F ₂₂	F ₃₃	F ₄₄	F ₅₅	F ₆₆	F ₇₇	F ₈₈	F ₉₉	
A' 2330	21.88	.102	-.420	1.15	-.145	-.018	-.007	.009	.139	76.3(1) + 21.9(4)
1756		14.00	1.23	-.168	.017	1.25	.201	.495	-.012	47.0(2) + 19.4(8) + 14.0(7) + 11.2(3)
1190			6.05	.546	.856	.785	-.380	-.121	.021	34.2(7) + 25.4(8) + 20.4(3) + 11.7(6)
1057				5.93	1.04	-.104	-.033	-.381	.246	28.7(6) + 24.3(4) + 21.9(7)
913					1.60	.047	-.069	-.081	.088	35.2(5) + 27.2(8) + 16.5(9) + 12.3(4)
690						5.140	.159	-.600	.028	37.3(7) + 32.0(9) + 14.9(6) + 13.3(5)
526							1.35	.077	-.002	49.4(7) + 39.3(9)
477								1.27	.003	66.2(9) + 30.0(8)
186									.413	68.6(9) + 22.0(5)
A'' 701	F _{10,10} .803	F _{11,11} -.008	F _{12,12} -.088							68.6(10) + 28.6(12)
514		.021	.006							96.5(11)
162			.121							62.1(11) + 37.9(12)

[a] Stretching constants in mdyne/Å, deformation constants in mdyne-Å/rad², and stretch-bend interaction constants in mdyne/rad.

[b] PED in percent. Coordinates contributing less than 10 percent are omitted. Coordinates defined as follows (normalization factors are omitted): S₁ = ν(N₄-N₅), S₂ = ν(N₂-O), S₃ = ν(N₂-N₃), S₄ = ν(N₃-N₄), S₅ = δ(N₂-N₃-N₄), S₆ = ν(N₂-F), S₇ = 2δ(F-N₂-O) - δ(F-N₂-N₃) - δ(O-N₂-N₃), S₈ = δ(F-N₂-N₃) - δ(O-N₂-N₃), S₉ = δ(N₃-N₄-N₅), S₁₀ = ω(O-N₂-N₃-N₄) - ω(F-N₂-N₃-N₄), S₁₁ = ω(N₂-N₃-N₄-N₅), S₁₂ = ω(O-N₂-N₃-N₄) + ω(F-N₂-N₃-N₄).

Table 4. Results from the normal coordinate analysis of $z\text{-N}_3\text{NOF}^+$ at the B3LYP/cc-pvtz level

calcd freq, cm^{-1}	symmetry force constants ^a									PED [%] ^b
	F ₁₁	F ₂₂	F ₃₃	F ₄₄	F ₅₅	F ₆₆	F ₇₇	F ₈₈	F ₉₉	
A' 2332	21.82	-.058	-.414	1.15	-.148	.130	.003	.049	.156	75.7(1) + 22.5(4)
1842		15.140	1.36	-.086	.033	1.23	.152	.486	.019	46.9(2) + 24.2(8) + 13.3(7)
1209			6.34	.563	1.02	.721	-.419	.120	.005	41.5(3) + 27.8(7) + 15.2(4)
1027				6.25	1.01	-.128	-.038	.227	.224	37.2(8) + 20.0(5) + 17.8(7) + 11.5(4)
764					1.72	.114	-.176	-.094	.029	47.5(6) + 17.4(9)
701						3.71	.174	-.536	.004	41.2(9) + 26.4(5) + 25.8(7)
562							1.33	.080	.012	60.0(7) + 17.8(8) + 14.4(6)
456								1.28	.028	71.5(9) + 22.6(8)
196									.440	68.2(9) + 22.5(5)
A'' 687	F _{10,10} .786	F _{11,11} .008	F _{12,12} .074							64.1(10) + 35.9(11)
498		.023	.006							96.2(11)
148			.098							45.3(11) + 54.4(12)

[a] and [b], see footnotes of Table 3.

Figure 1. Structures of z -N₃NFO⁺ and e -N₃NFO⁺ calculated at the CCSD(T)/6-311G(2df) level of theory (bond lengths in Å, bond angles in degree).

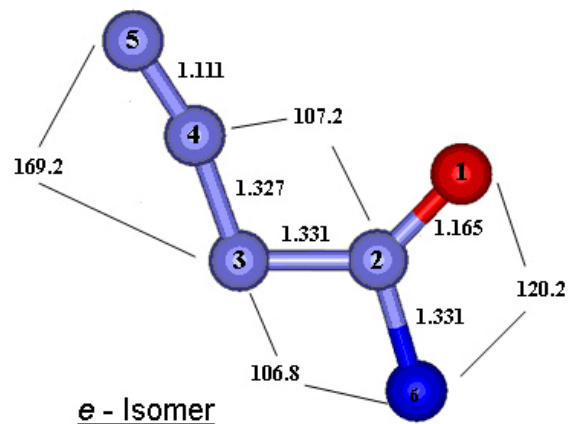
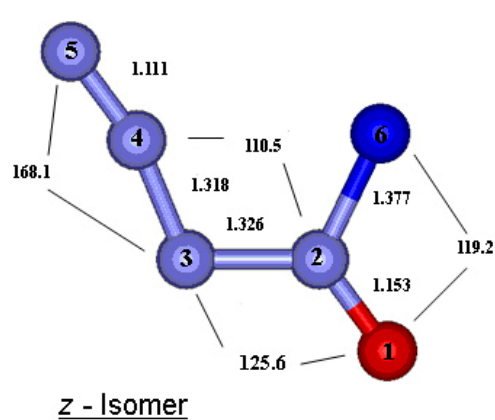
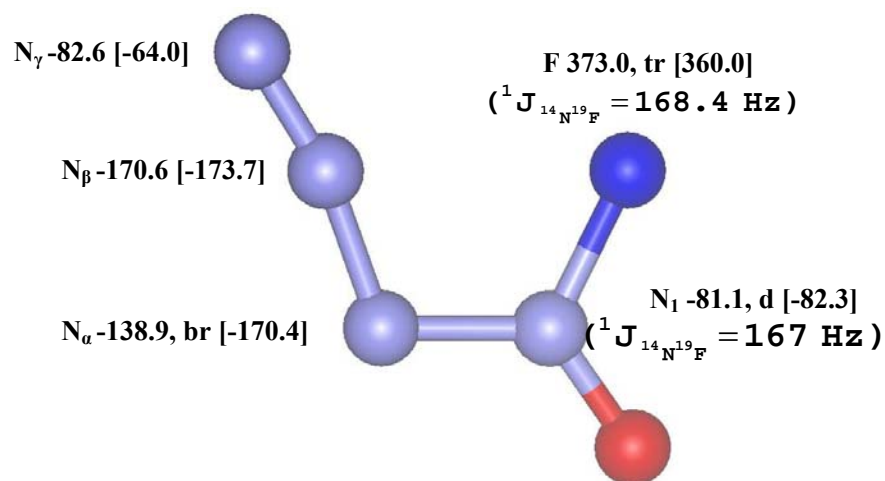
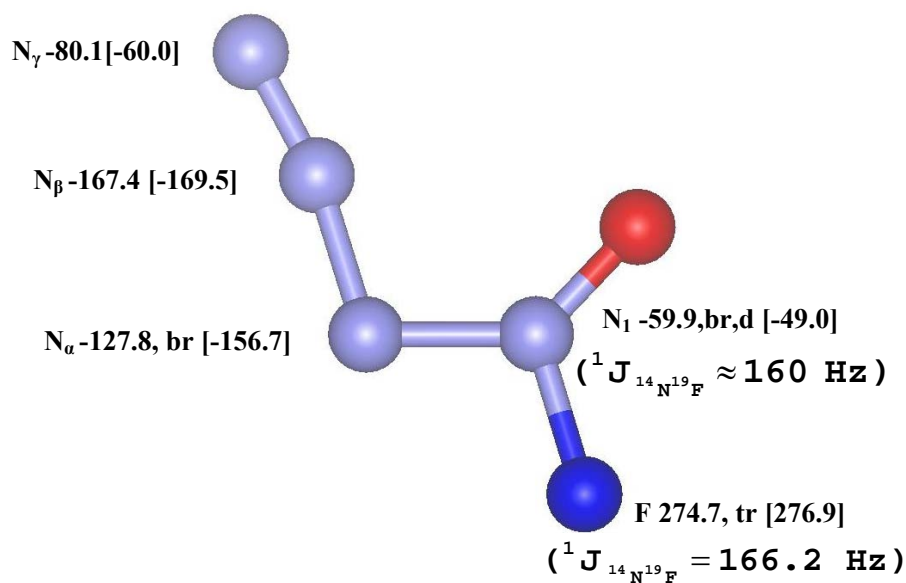


Figure 2. Multinuclear NMR parameters of z -N₃NFO⁺ and e -N₃NFO⁺ (chemical shifts in ppm and coupling constants in Hz). The values predicted at the PBE1BPE/6-311+G(2df) level are shown in brackets.



z-Isomer



e-Isomer

Figure 3. Plot of the nitrogen chemical shifts of $z\text{-N}_3\text{NFO}^+$, $e\text{-N}_3\text{NFO}^+$ and related X-N_3 type covalent azides arranged according to increasing electronegativity of the X-group; \blacklozenge N_α , \blacksquare N_β , \blacktriangle N_γ , \circ N_1 .

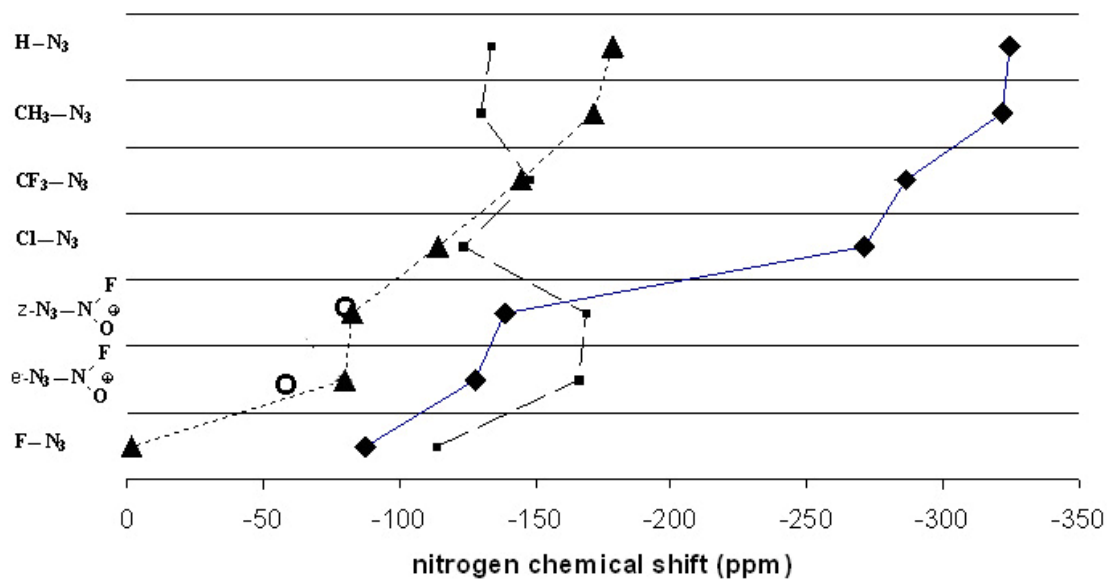
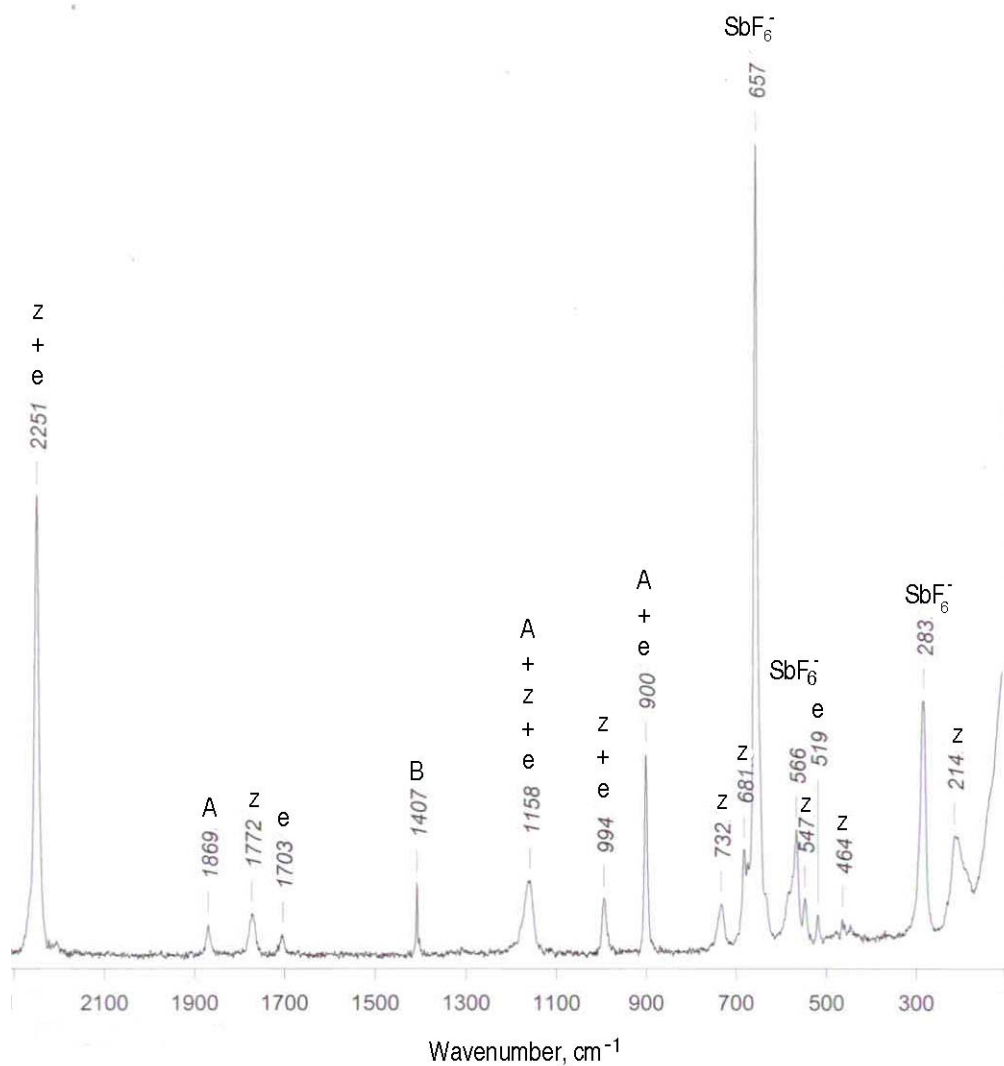


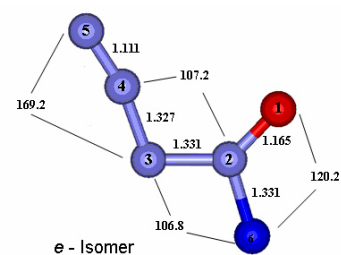
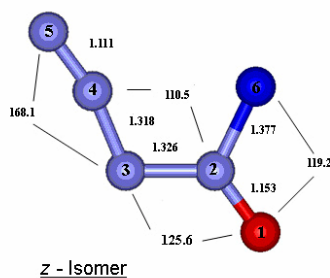
Figure 4. Typical Raman spectrum of a mixture of solid $z\text{-N}_3\text{NFO}^+\text{SbF}_6^-$ and $e\text{-N}_3\text{NFO}^+\text{SbF}_6^-$, containing some $\text{NF}_2\text{O}^+\text{SbF}_6^-$ (A) and $\text{NO}_2^+\text{SbF}_6^-$ (B) as impurities.



Synopsis

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Synthesis and Characterization of *z*- N_3NFO^+ and *e*- N_3NFO^+



New stable nitrogen fluoride oxide ion: The second known example of a stable nitrogen fluoride oxide ion, N_3NFO^+ , was prepared as its SbF_6^- salt and characterized by multi-nuclear NMR and vibrational spectroscopy and electronic structure calculations. The cation is planar and exists as two stereo isomers.